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23Na NMR study of sodium order in Na xCoO 2 with 22 K Néel temperature

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Abstract

We report a systematic study of the c-lattice parameter in the Na xCoO 2 phases versus Na content x>0.5, in which sodium always displays ordered arrangements. This allows us to single out the first phase which exhibits an antiferromagnetic order at a Néel temperature T N=22 K, which is found to occur for x0.77(1). Pure samples of this phase have been studied both as aligned powders and single crystals. They exhibit identical 23Na NMR spectra in which three sets of Na sites could be fully resolved, and are found to display T dependencies of their NMR shifts, which scale with each other. This allows us to establish that the T variation of the shifts is due to the paramagnetism of the Co sites with formal charge state larger than 3 +. The existence of a sodium site with axial charge symmetry and the intensity ratio between the sets of 23Na lines permits us to reveal that the two-dimensional structure of the Na order corresponds to ten Na sites on top of a thirteen-Co-sites unit cell, that is with x=10/130.77. This structure fits with that determined from local density calculations and involves triangles of three Na sites located on top of Co sites [so-called Na1 sites]. The associated ordering of the Na vacancies is quite distinct from that found for x<0.75.

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